

NO DRAWINGS

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(54) PRODUCTION OF POLYMERIC POLYETHERS AND POLYTHIOETHERS

(71) We, CELANESE CORPORATION, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

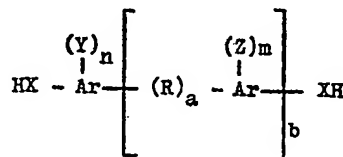
This invention relates to the production of polymeric polyethers and polythioethers.

Polymeric polyethers and polythioethers exhibit toughness and stability at high temperatures and accordingly are useful, especially in sheet or film form, in applications where polyacetals and polycarbonates are commonly used. The polyethers have been made by preparing the alkali metal salt of a dihydric phenol and then reacting it with a dihalobenzenoid compound. However, in this process it is essential to use the stoichiometric amount of alkali, e.g. potassium hydroxide or sodium methoxide, when making the phenol salt since any excess causes hydrolysis in the polyether production with loss of halogen from the dihalobenzenoid compound and formation of a product of undesirably low molecular weight. The molecular weight of the polyether is also lowered by the presence of free phenol resulting from the use of too little alkali in making the phenol salt and by the presence of water which is formed in making the phenol salt and the removal of which necessitates the use of azeotropic distillation. The present invention is concerned with a process for the production of polyethers and polythioethers by which these difficulties can be avoided and a product obtained of consistent molecular weight.

According to the invention, a polymeric polyether or polythioether is produced by subjecting an aromatic compound containing two —XH groups in which X is oxygen or sulphur, or a mixture of two or more such compounds, to reaction with one or more dihalobenzenoid compounds in a polar solvent sufficient in quantity to dissolve the reagents and the polymeric product and in presence of potassium carbonate.

It is best to employ a high boiling polar solvent, e.g. one having a boiling point above 100°C. Examples of such polar solvents are dimethylsulphoxide, diethylsulphoxide, tetramethylene sulphoxide, diphenylsulphone, dimethylsulphone, diethylsulphone, di-isopropylsulphone, hexamethylphosphoramide, diethylene glycol, dimethylacetamide, dimethylformamide and nitrobenzene, the preferred solvent being dimethylformamide. It will be understood that mixtures of solvents may be employed.

The aromatic compound containing two —XH groups may be a compound having the following structure:—

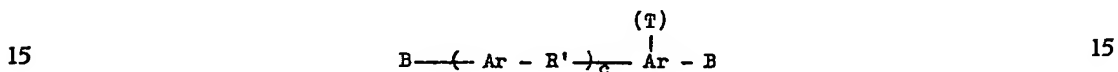


wherein X is an oxygen or a sulphur atom, Ar is an aromatic radical containing 6 carbon atoms, Y and Z are the same or different inert substituents, e.g. alkyl or alkoxy groups containing from 1 to 4 carbon atoms or halogen atoms, n and m are zero or

integers from 1 to 4, R is a divalent radical, e.g. $\overset{\text{O}}{\parallel}\text{C}$ —, —O—, —S—, —S—S— or SO₂ or a hydrocarbon group containing from 1 to 8 carbon atoms and a and b are each either 0 or 1.

5 Examples of such compounds which may be employed are the dihydroxy and dimercapto derivatives of the bisphenyl alkanes, e.g. 2,2-bis(4-hydroxyphenyl) propane; 2,2-bis(4-mercapto phenyl) propane; 1,1-bis(4-hydroxy-2-chlorophenyl) ethane; 1,1-bis(4-mercapto-2-chlorophenyl) ethane and bis(4-hydroxy-2,6-dimethyl-3-methoxyphenol); bis(4-hydroxyphenyl) sulphone; bis(4-mercaptophenyl) sulphone; bis(4-hydroxyphenyl) ether; bis(4-mercaptophenyl) ether; bis(4-hydroxyphenyl) carbonyl; 10 bis(4-mercaptophenyl) carbonyl; 4,4'-biphenyldithiol; p,p'-benzenedithiol; and dihydroquinone. Particularly preferred as a starting material is Bisphenol A, i.e. 2,2'-bis(4-hydroxyphenyl) propane.

The dihalobenzenoid compound should have at least one halogen atom bonded to a benzene ring and may have the following structure:—



wherein B is halogen, Ar is an aromatic radical containing 6 carbon atoms, c is either 0 or 1 and R' is an electron withdrawing group which is chemically inert in the process. The higher the capacity the R' group has for electron withdrawing, the faster the reaction will proceed as the halogens are relatively less hindered under reaction conditions so that the group may be termed an activator group. R' may be, for instance, —SO₂—, —CO—, —C=C—, —SO—, —N=N—, or a hydrocarbon or substituted hydrocarbon group containing from 1 to 4 carbon atoms. (T) is a substituent mono-valent activator group, for instance a nitro, phenylsulphone, alkyl sulphone containing from 1 to 6 carbon atoms, cyano, trifluoromethyl or nitroso groups or a group containing heterocyclic nitrogen, e.g. a pyridine residue, and is present only when c is 0. A preferred example of dihalobenzenoid compound where c is 0 is 2,4-dichloronitrobenzene. Preferred dihalobenzenoid compounds where c is 1 are 4,4'-dichlorodiphenyl sulphone, difluorodiphenylsulphone and 4,4'-difluorobenzophenone.

30 The invention is particularly concerned with the production of a polymer by reacting a single compound containing a pair of —XH groups, X being oxygen or sulphur, with a single dihalobenzenoid compound but more than one of either or both kinds of reactant may be used, for example the polymer may be one made by reacting together Bisphenol A, p,p'-bisphenol and 4,4'-dichlorodiphenylsulphone.

35 The reaction is generally carried out at temperatures of from 80°C. up to the boiling point of the solvent employed and, preferably, from 100°C. to 5°C. below the boiling point of the solvent. For instance, when dimethylformamide (bp 153°C.) is employed, the reaction temperature may be from 80°C. to 153°C. and preferably from 100°C. to 148°C.

40 The reaction mixture is heated for a time sufficient to produce the desired product, which may, in general, be for from 1 hour to 24 hours. The process is preferably carried out at atmospheric pressure but subatmospheric pressure or superatmospheric pressure may be employed if desired.

45 The monomer reactants are preferably used in equimolar ratios although the use of molar ratios differing by up to 5% from the equimolar amounts does not appear to have any substantial effect on the product.

50 The solvent is present in sufficient quantity to dissolve substantially all of the monomer reactants and the polymer product which is subsequently formed. Usually an amount of solvent equal to 5 to 15 molar proportions per molar proportion of the reactants present is satisfactory. Less solvent is usually necessary if an extremely strongly polar solvent is employed than if a less strongly polar solvent is used.

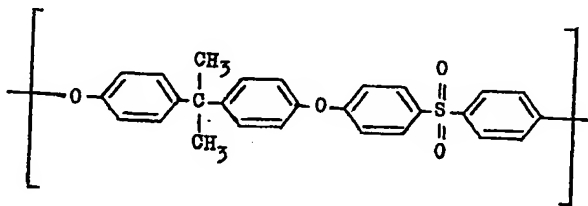
55 The potassium carbonate is preferably anhydrous and is added to the reactants in a sufficient amount to complete the reaction and, preferably, in amount equal to the total amounts of reactants present on a molar basis, e.g. with one molar part each of Bisphenol A and 4,4'-dichlorodiphenyl sulphone there are used two molar parts of potassium carbonate. Less than equimolar amounts may be employed but in this case the molecular weight of the final product will be lower than might be desired. However, up to 20% or even somewhat higher molar excess of potassium carbonate may be

employed without substantially affecting the properties of the final product. The use of anhydrous potassium carbonate prevents the generation of water and thus avoids the necessity of using an azeotropic distillation step as in the prior process referred to; it will also be noted that the use of an exactly stoichiometric amount of potassium carbonate is unnecessary. It is believed that, since the potassium carbonate is only slightly soluble in the solvent, this compound is in effect metered into the solution during the process and consequently a relatively large excess of the compound may be added to the reaction vessel initially without untoward effect.

The following Examples illustrate the invention: —

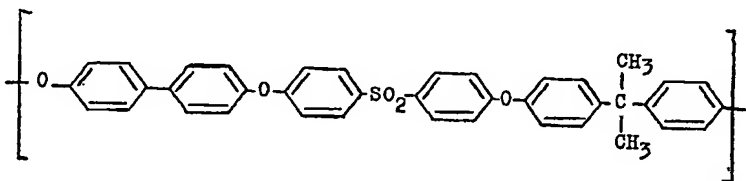
EXAMPLE 1

Into a 500 millilitre, 3-necked, round bottomed flask fitted with a U-shaped Claisen adapter, heating mantle, mechanical stirrer, condenser, thermowell and fritted glass nitrogen inlet tube there were introduced 22.83 grams (0.1 mole) of 2,2'-bis(4-hydroxyphenyl)propane, 28.72 grams (0.1 mole) of 4,4'-dichlorodiphenylsulphone, 31.79 grams (0.2 mole + 15% molar excess) of anhydrous potassium carbonate and 100 millilitres of dimethylformamide. The mixture was heated to 140°C. and kept at that temperature for 24 hours. The reaction mixture was cooled to room temperature and 500 millilitres of dichloromethane then added. The undissolved salts were filtered off and the dichloromethane solution was then washed with 500 millilitres of water containing 10 millilitres of concentrated hydrochloric acid. The organic layer was separated and added slowly to 1500 millilitres of boiling water to precipitate the polymer. The polymer was filtered off and then dried in a vacuum oven at 120°C. for 24 hours. The polymer thus produced had an I.V. (in chlorobenzene) of 0.30 to 0.33, a reduced viscosity (in chloroform) of 0.56 to 0.58, a melt index at 300°C. of 1.75 grams per 10 minutes and a melting point of 218°C. to 222°C. Infra-red analysis indicated that the polymer comprised the following repeating unit: —



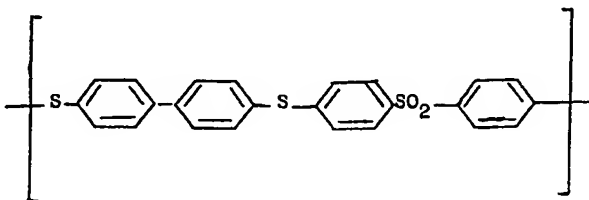
EXAMPLE 2

Example 1 was repeated with the exception that a 50:50 blend of Bisphenol A and p,p'-bisphenol (0.1 mole) was reacted with 4,4'-dichlorodiphenylsulphone (0.1 mole). The polymer produced had an I.V. (in chlorobenzene) of 0.42, a reduced viscosity (in chloroform) of 0.44, a melt index at 300°C. of 4.8 grams per 10 minutes and a melting point of 225° to 229°C. Infra-red analysis indicated that the polymer comprised the following repeating unit: —



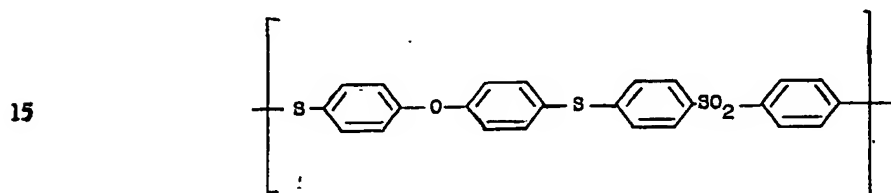
EXAMPLE 3

Into a 500 millilitre, 4-neck, flask equipped with an overhead mechanical stirrer, reflux condenser with nitrogen inlet tube and thermowell there were introduced 21.83 grams (0.10 mole) of 4,4'-biphenyldithiol, 28.72 grams (0.10 mole) of 4,4'-dichlorodiphenylsulphone, 31.79 grams (0.23 mole + 15% molar excess) of anhydrous potassium carbonate and 200 millilitres of N,N-dimethylformamide. The mixture was heated to 150°C. for 24 hours and then cooled to room temperature and treated with 300 millilitres of dichloromethane. Complete precipitation of the polymer was caused by the addition to the dichloromethane mixture of 1500 millilitres of boiling de-ionized water with subsequent filtration. The polymer was then dried in a vacuum oven at 150°C. for 16 hours. Infra-red analysis indicated that the polymer comprised the following repeating unit: —



EXAMPLE 4

Into a 250 millilitre, 3-necked, flask equipped with a U-tube adapter with re-
flux condenser and nitrogen inlet tube, overhead mechanical stirrer and thermowell
there were introduced 8.00 grams (0.034 mole) of 4,4'-biphenyletherdithiol, 9.76 grams
(0.034 mole) of 4,4'-dichlorodiphenylsulphone, 10.78 grams (0.078 mole + 15% molar
excess) of anhydrous potassium carbonate and 100 millilitres of dimethylformamide.
The mixture was heated to 150°C. for 24 hours and the resulting yellow mixture
was cooled to room temperature and treated with 100 millilitres of dimethylformamide.
Precipitation of the polymer was caused by adding the dimethylformamide solution
to 750 millilitres of boiling de-ionized water. The white product was filtered and
treated again with 750 millilitres of boiling de-ionized water with subsequent filtra-
tion. The polymer was then dried in a vacuum oven at 150°C. for 16 hours. Infra-
red analysis indicated that the polymer comprised the following repeating unit:—

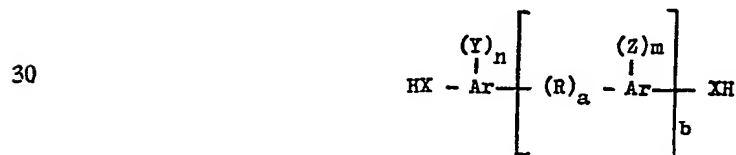


It should be noted that, in the process of the invention, omission of the potas-
sium carbonate, or its replacement by other kinds of substance which might be thought
likely to promote the desired reaction, e.g. piperidinium acetate, ammonium acetate
and triphenylmethylantimony hexafluoride or acid acceptors, e.g. pyridine or quinoline,
gives a product consisting of unchanged starting materials.

WHAT WE CLAIM IS:—

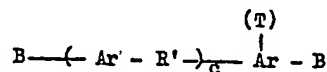
1. Process for the production of a polymeric polyether or polythioether, which
comprises subjecting an aromatic compound containing two —XH groups in which
X is oxygen or sulphur, or a mixture of two or more such compounds, to reaction with
one or more dihalobenzenoid compounds in a polar solvent sufficient in quantity to
dissolve the reagents and the polymeric product and in presence of potassium car-
bonate.

2. Process according to Claim 1, wherein said aromatic compound containing two
—XH groups has the following structure:—



wherein X is an oxygen or a sulphur atom, Ar is an aromatic radical containing 6
carbon atoms, Y and Z are the same or different inert substituents which are alkyl
or alkoxy groups containing from 1 to 4 carbon atoms or halogen atoms, R is a di-
valent radical which is —CO—, —O—, —S—, —S—S—, SO₂ or a hydrocarbon
group containing from 1 to 8 carbon atoms, a and b are each 0 or 1 and m and n are
zero or integers from 1 to 4.

3. Process according to Claim 1 or 2, wherein said dihalobenzenoid compound has the following structure:—



- 5 wherein B is halogen, Ar is an aromatic radical containing 6 carbon atoms, R' is a di-
valent radical which is $\text{—SO}_2\text{—}$, —CO— , —C=C— , —SO— , —N=N— , or a
hydrocarbon or substituted hydrocarbon group containing from 1 to 4 carbon atoms,
(T) is a substituent monovalent radical which is nitro, phenylsulphone, alkylsulphone
10 containing from 1 to 6 carbon atoms, cyano, trifluoromethyl or nitroso group or a
group containing heterocyclic nitrogen, c being 0 or 1 and (T) being present only
when c is 0. 10
4. Process according to Claim 1, 2 or 3, wherein said potassium carbonate is an-
hydrous.
5. Process according to Claim 1, 2, 3 or 4, wherein the aromatic reactants are
present in substantially equimolar amounts.
- 15 6. Process according to Claim 3, wherein said aromatic compound is Bisphenol
A, 4,4'-diphenyldithiol or 4,4'-diphenyletherdithiol. 15
7. Process according to Claim 3, wherein said dihalobenzenoid compound is 4,4'-
dichlorodiphenylsulphone.
- 20 8. Process for the production of a polymeric polyether or polythioether accord-
ing to Claim 1 and substantially as hereinbefore described. 20
9. Polymeric polyethers and polythioethers, whenever produced by any of the
processes claimed in the preceding claims.

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